

# Compositing and Sub Sampling of Media Related to Waste Management Activities

Susan D. Gagner and Alan B. Crockett

This was prepared for submittal to the  
*12th Annual Waste Testing and Quality Assurance Symposium*  
*Washington, D.C.*  
*July 22-24, 1996*

May 1996



Lawrence  
Livermore  
National  
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

#### DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

## **COMPOSITING AND SUBSAMPLING OF MEDIA RELATED TO WASTE MANAGEMENT ACTIVITIES**

Authors: Susan D. Gagner, Sampling Group Supervisor, Hazardous Waste Management, Lawrence Livermore National Laboratory, 7000 East Ave.,  
L-311, Livermore, CA 94550, Alan B. Crockett, Consulting Scientist/Engineer, Lockheed Martin Idaho Technologies, Idaho National Engineering Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-2213

### **ABSTRACT**

The American Society for Testing and Materials (ASTM) has been working with the U.S. Environmental Protection Agency (EPA) to develop methods for use in the Environmental RCRA/CERCLA program. Two standards being developed are guides to field compositing and laboratory subsampling.

Correctly performed compositing and subsampling are critical in the chain of sampling and analytical events. They must be accomplished in compliance with project objectives and instructions to assure that the resulting data is representative. In a site characterization effort, the collection of composite samples may be used to estimate the mean concentration of a waste analyte in contaminated media. Other reasons to composite include reducing costs, efficiently determining the absence or possible presence of a hot spot, and, when coupled with retesting schemes, locating hot spots. If composite samples are collected, it is necessary to ensure that a representative sample is obtained for analysis. This may mean that samples must be mixed and subsampled using procedures that could include pan mixing and quartering, a mixing square, kneading, sieving and mixing, and particle size reduction. Field subsampling procedures include use of a rectangular scoop, an alternate scoop technique, and the slab-cake methods.

A significant source of analytical error exists in obtaining a representative subsample of a sample delivered to a laboratory. Techniques for obtaining representative subsamples include homogenization, layer analysis, grinding and sieving, mixing, transversal subsampling, cone and quartering, riffing, use of a mixing square, use of mechanical mixers, and particle size reduction. Other techniques include changing the physical state such as digesting, drying, melting or freezing. These methods can be applied to a variety of matrices including solid wastes, single-phased liquids, sludges, and multilayered samples. These techniques are dependent on sample matrix, the type of analysis performed, the characteristic of interest, and the project specific instructions. These subsampling methods are designed to reduce the three major sources of subsampling errors; fundamental errors, grouping and segregation errors, and materialization errors.

Both of these guides are still in the developmental stages at ASTM.. They should soon be available for general use.

### **INTRODUCTION**

Data Quality Objectives are generally dependent on getting data that is representative of the site. The more heterogeneous the site matrix, the more difficult this is to achieve. Two areas that influence the ability to achieve a representative sample are compositing in the field, and subsampling in the laboratory. Due to the lack of regulatory guidance in these areas, the EPA asked ASTM to write standards addressing compositing and subsampling as part of a cooperative agreement between these agencies.

### **COMPOSITING**

Composite sampling (compositing) is the combining of two or more samples into one. The principle assumption in the decision to composite is that the analytical costs are high relative to the sampling costs. The reasons to composite include:

- improving the precision mean estimation
- reducing costs associated with analysis
- efficiently determining the absence or presence of a hot spot
- when coupled with retesting schemes, locating hot spots
- providing a degree of anonymity where population statistics are necessary.

When estimating the mean concentration, a set of composite samples from a heterogeneous population always provides a more precise estimate of the mean than a comparable number of discrete samples. This is because of the physical process of averaging that occurs which provides a greater level of statistical confidence. The composite samples tend to be more normally distributed than the individual samples. This is an advantage for compositing, since the calculation of the mean, standard deviation, and confidence levels generally assumes the data is normally distributed. Spatial design of the compositing scheme is also important, since compositing can either help determine the spatial variability of a site, or be used to improve the precision of the parameter of interest across the whole site.

Due to the increased precision of compositing, the number of composite samples required to achieve a specified precision is smaller than that required for individual samples. The higher the analytical costs relative to the sampling and compositing costs, the greater the savings to the project budget.

Samples can be composited to determine whether an individual sample exceeds a specified limit as long as the action limit is relatively high compared with the actual detection limit and the average sample concentration. For example, if a site was being analyzed for PCB, the known analytical detection limit is  $<5$  mg/kg of soil, and the action level is 50 mg/kg, then up to 10 samples could be composited to determine if any of the samples are a "hot spot." Depending on the difficulty and probability of having to resample, it may be desirable to retain a split of the discrete samples for possible re-analysis to find the specific spot. This type of composite sampling can only be used as a cost saving measure if the possibility of finding a hot spot is relatively low ( $<40\%$ ).

The principle limitation of compositing is the loss of discrete information achieved from a single sample. However, the following situations may not lend themselves to cost-effective compositing either:

- when the integrity of the individual sample values change due to compositing (e.g., chemical reactions occur between constituents in the samples being combined, or volatiles lost during mixing)
- where the composite sample cannot be properly mixed and subsampled in the field or the whole composite cannot be analyzed
- when the goal is to detect hot spots and a large proportion of the samples are expected to test positive for the characteristic of interest
- when analytical costs are low relative to sampling costs (e.g. field testing equipment)
- when regulations specify that a grab sample must be collected.

In general, the individual samples to be composited should be of the same mass. However, proportional sampling may be appropriate in some cases, depending upon the objective. For example, if the objective is to determine the average contaminant concentration of the waste contained in a group of drums, the volume of each sample to be composited should be proportional to the amount of waste in the drum. Another example would be in estimating the contaminants concentration of soil overlaying an impermeable layer. Soil cores should be collected and composited from the surface to the impermeable layer, regardless of the core length

Frequently, it is necessary to mix an individual or composite sample and obtain a representative subsample(s) for transport to an analytical lab. Even when the entire sample collected is to be submitted to the laboratory, it may be desirable to thoroughly mix the sample to help assure that the laboratory analyzes or extracts a representative aliquot. The thoroughness of mixing needed for subsampling is a function of the proportional size of the subsample. The principle problem is that the smaller the aliquot, the less representative the aliquot may be, unless it is thoroughly

mixed, homogenized and subsampled. Compositing samples without adequate mixing can nullify the potential benefits of compositing. Prior to mixing, project specific instructions (e.g., the sampling and analysis plan) should be followed.

Methods that may be applicable to field mixing are dependent on matrix. This includes field mixing and quartering in a pan, sieving, kneading, grinding, particle size reduction, and other mixing equipment (e.g., riffle splitters, cone and quartering, etc.). While it is not always possible to determine if a sample is adequately mixed, following standard operating procedures and observing sample texture, color, and particle size distribution are practical methods. If samples are sieved or large materials are removed, it may be necessary to record the mass of materials removed for later estimation of contaminant concentrations in the original sample.

Once the composite sample is mixed, it may need to be subsampled. The reasons for this include a composite sample that is larger than the sample container, or the need to split the composite into multiple sample bottles. If mixing procedures could assure a homogenous sample, subsampling in the field would be simple. However, particles may segregate according to size during mixing, and improper subsampling would introduce bias. Since homogeneity cannot be assumed, appropriate subsampling procedures in the field should be used by field personnel to achieve representative samples. Methods for field subsampling include riffle splitters, cone and quartering, rectangular scoop, alternate scoop, and slab cake techniques.

### **LABORATORY SUBSAMPLING**

Sources of uncertainty arise from sample heterogeneity and from the actual subsampling procedure used. There are three general sources of error that pertain to the subsampling of environmental samples. These must be understood before choosing a subsampling method. These include:

- fundamental error
- grouping and segregation error
- materialization error.

Fundamental error occurs when the contaminants of interest exist as particles or are attached to particles that are randomly dispersed throughout the matrix while the matrix itself is not contaminated or is contaminated with much lower concentrations of the contaminant of interest. The measured concentration of contaminant in such a waste will depend upon the number of these particles that are in the specimen subjected to analysis. For a given concentration, the greater the particle size, the fewer contaminated particles there are in the subsample, hence the smaller the chance is that the contaminant will be appropriately represented in the specimen.

Grouping and segregation error is a function of the distribution of unlike particles (i.e., size, shape, density) within a sample. Differences in size, shape and density can affect heterogeneity further by the development of different strata upon agitation or vibration of the sample.

Materialization errors are those that result from using incorrect subsampling devices or from the incorrect use of subsampling devices.

Successful implementation of laboratory subsampling depends on effective communication between the data user and the laboratory staff. The selection of optimal procedures by the laboratory depends on the intended use of the data. The data user should submit appropriate instructions with all samples and, when necessary, the laboratory staff should contact the data user for confirmation or further clarification of these instructions. Options should be discussed before initiating any subsampling procedure. These options include:

- removal of artifacts, such as rocks and twigs, from the sample prior to subsampling
- digesting or extracting the contaminant from the outside of the large particles instead of breaking down the entire particle
- digesting or extracting particle sizes separately

- using or forming an emulsion layer so that the material may be treated as a single layer
- separation of layers
- drying the sample
- changing the physical state, such as freezing the material so that it may be treated as a solid, or melting the material so that it may be treated as a liquid
- analysis of only one layer of multilayered samples, such as analyzing only the oil portion of an oil/water mixture for PCBs
- compositing portions of a sample for volatile analysis directly in a purge unit vs individual analysis of these portions
- choice of standard method for solids, such as grinding, mixing, cone and quartering, riffing, sieving, or particle size reduction.

Sampling theory suggests a minimum sample size that increases as the size of the largest particle increases. Often, these minimum sample sizes are larger than the normal sample sizes subjected to environmental analysis. Sometimes, the analytical subsample can be increased, or the size of the subsample subjected to digestion or extraction can be increased and a smaller subsample of the well mixed digestate or extract can be submitted for analysis. Another approach involves dividing a sample of the requisite size into smaller subsamples, which can be subject to preparation. The resulting digestates or extracts can be analyzed individually or proportionally re-composited and a composite sample analyzed.

Subsampling techniques are different when analyzing for volatile compounds than non-volatile compounds. The differences are included for each sample matrix.

#### I. Solid Matrices

If the maximum particle size is too large for the specimen used in the laboratory, sampling theory would suggest that either particle size reduction is used, or a larger sample size is digested. If something is known about the scale of the “Contaminant Unit” and the mechanism of contamination, the use of particle size reduction may be avoidable. If the contaminant unit is on the atomic or molecular scale or is a particle much smaller than the maximum particle size of the sample, then alternative approaches can be employed with acceptable bias.

For volatile analyses, the Table 1 sums the alternative subsampling methods, since particle size reduction is not possible.

	Particle Size of Sample	Contaminant Unit in Sample	Subsampling Method
Method A	< Maximum Particle Size Allowed	< Maximum Particle Size Allowed	Mix with minimum disturbance, weigh specimen, place in appropriate solvent.
Method B	> Maximum Particle Size Allowed	< Maximum Particle Size Allowed	<p>If data user can accommodate false high concentration, subsample only smaller particles.</p> <p>Another method is to extract the sample with the appropriate solvent, and analyze the solvent as a single phase.</p>

Method C	> Maximum Particle Size Allowed	> Maximum Particle Size Allowed	An alternative to particle size reduction is to use larger sample sizes, dividing the total amount into manageable sizes, then combine the extracts into the same purge chamber.
----------	---------------------------------	---------------------------------	--

Table 1. Subsampling Solids for Volatile Analysis

For non-volatile analysis, Table 2 sums the subsampling methods. Gelatinous samples, such as asphalt, may be cooled with dry ice or liquid nitrogen. This makes it possible to grind gelatins and other semi-solids. It is also important to be knowledgeable about the limitations on each of these subsampling methods.

	Particle Size of Sample	Contaminant Size in Sample	Subsampling Methods
Method D	< Maximum Particle Size Allowed	< Maximum Particle Size Allowed	Transversal Subsampling  Cone and Quartering  Riffle Splitter  Grinding and Sieving  Mechanical Methods (e.g., spiral mixer, cement mixer, twin-shell V blender, or mills)
Method E	> Maximum Particle Size Allowed	< Maximum Particle Size Allowed	If the data user can accommodate false high concentrations, large particles can be removed, and the methods listed in Method D may be used.
Method F	> Maximum Particle Size Allowed	> Maximum Particle Size Allowed	Particle Size Reduction, using such devices as cutting mills, micro-mills, grinding mills, or jar mills.  Another method is to use larger sample sizes by extracting or digesting several aliquots. The extracts or digestates may be analyzed separately and the results can be weight-averaged, or the extracts or digestates may be combined prior to analysis.

Table 2. Subsampling Solids for Non-volatile Analyses

## II. Single-phased Liquids

Aqueous samples for non-volatile compounds may contain settleable solids. If the settleable materials are to be considered part of the sample, they must remain in suspension, or be able to be re-suspended and remain so during the subsampling operation. These samples are then treated as a single-phase liquid. These samples should be gently swirled for 15 seconds or slowly inverted 6 times to assure homogenization. If the settleable materials are not considered to be part of the sample, the liquid subsample or specimen may be obtained by filtering, centrifuging, or decanting the liquid portion from the solid portion. The liquid portion can also be pipetted directly into the analytical vessel.

For volatile compounds, samples should not be mixed prior to subsampling. For low concentration materials, the specimen is pipetted straight into the syringe barrel. For high levels of contaminants, use a microliter syringe to collect the specimen directly, or transfer the subsample into a solvent appropriate for analysis in an air-tight container (dilution process).

## III. Sludge

Laboratory samples with significant solids cannot be mixed vigorously enough to suspend a solid phase without the potential of losing volatile components. One method of handling sludge is to freeze it, and then handle it as a solid. Generally, the most practical method is to separate them out into their component phases.

For non-volatile compounds, the liquid subsample can be obtained by filtering, centrifuging, decanting, or by pipetting out only the liquid phase from a solution that has settled. Prior to starting, determine the percentage of the phases either by volume or by weight. After separating the liquid from the solid, analyze separately, and weight average the results.

For volatile compounds, gentle centrifuging, or settling can be used to separate the phases. After the liquid subsample is removed, using the methods described in single-phased liquids, the liquid is decanted into a separate container. The solid phase can then be weighed and added directly on the purge unit as quickly as possible.

## IV. Multilayered Samples

Multilayered samples are those with two or more distinct visual layers of material. These layers may be the result of differences in density, such as liquid/liquid layers (e.g., chlorinated solvents and water, or water and oil), liquid/solid layers (e.g., sludge), solid/solid layers (e.g., small rocks and large rocks), or combinations of these layers (e.g., water, oil, and dirt). These layers may also be the result of depositional layering, such as green clay and sandy loam from a coring sample.

The methods used in the discussion on sludges will also work for multilayered samples. This includes the use of dry ice or liquid nitrogen to freeze the sample, or separating these samples into their component phases.

For liquid/liquid layers, a separatory funnel may be helpful in separating the phases, if the analysis is for non-volatile compounds. These phases can then be proportionally recombined in the analytical vessel. For volatile compounds, they can be recombined directly on the purge unit to form a representative sample.

One or more of the previous methods mentioned in this paper can be utilized to subsample a multilayered sample, depending on how many layers are encountered in the sample.

## **SUMMARY**

In a sampling plan, the collection of composite samples may be used to improve the estimation of the mean contaminant levels, reduce analytical costs, determine the absence or presence of a hot spot, and, when coupled with retesting schemes, locate hot spots. While discreet sample



information is lost in compositing, collection of multiple composite samples from a grid cell permits estimation of within cell sampling error. There are several mixing and field subsampling techniques available to ensure that the sample sent to the laboratory is representative of what is in the field..

After the field sample arrives at the laboratory, proper subsampling is a key to ensuring that the data meets the data quality objectives. Subsampling must be completed only after a review of the appropriate instructions, or after discussing the options with the data user. Subsampling should then proceed in a manner dependent on the sample matrix, the type of analysis required, and the characteristic(s) of interest.

### **ACKNOWLEDGEMENTS**

Work by Susan Gagner performed under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Work by Alan Crockett was funded under U.S. Department of Energy Idaho Operations Office Contract DE-AC07-94ID13223.

### **REFERENCES**

ASTM Draft Standard, subcommittee D34.01, New Standard Guide for Composite Sampling and Field Subsampling for Environmental Waste Management Activities

ASTM Draft Standard, subcommittee D34.01, Standard Guide for Laboratory Subsampling of Media Related to Waste Management Activities